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(71)Applicant : SUMITOMO METAL MINING CO LTD

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(72)Inventor : ABE TAKAYUKI

## (54) FERROELECTRIC THIN FILM CONSTITUTION BODY

## (57)Abstract:

**PURPOSE:** To obtain a ferroelectric thin-film constitution body having a ferroelectric thin film having the properly arranged c-axis direction perpendicular to the surface of a substrate regardless of the kind thereof even without using a conventional expensive MgO single crystal substrate in relation to a ferroelectric thin-film constitution body used in, e.g. a pyroelectric type infrared detecting element, an actuator or a nonvolatile and nondestructive memory.

**CONSTITUTION:** This ferroelectric thin-film constitution body is obtained by forming an oxide thin film of a Bi-based layer perovskite type crystal structure on a substrate so as to properly arrange the (c)-axis of the crystal axis in the direction perpendicular to the substrate surface and further forming a ferroelectric thin film having the perovskite type crystal structure represented by the general formula  $ABO_3$  (A denotes one or more of Bi, Pb, Ba, Sr, Ca, Na, K and rare earth elements; B denotes one or more of Ti, Nb, Ta, W, Mo, Fe, Co, Cr and Zr) on the resultant oxide thin film.

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(71)出願人 000183303

住友金属鉱山株式会社

東京都港区新橋5丁目11番3号

(72)発明者 阿部 能之

千葉県市川市中国分3-18-5 住友金属

鉱山株式会社中央研究所内

(74)代理人 弁理士 菅 直人 (外1名)

(54)【発明の名称】 強誘電体薄膜構成体

(57)【要約】

【目的】 例えば焦電型赤外線検出素子、アクチュエータ、不揮発性かつ非破壊性のメモリなどに用いる強誘電体薄膜構成体に係り、従来の高価なMgO単結晶基板を用いなくても、また基板の種類の如何にかかわらず、基板面に垂直にc軸の方向が揃った強誘電体薄膜を有する強誘電体薄膜構成体を提供する。

【構成】 Bi系層状ペロブスカイト型結晶構造の酸化物薄膜が、その結晶軸のc軸が基板面に対して垂直方向に揃うように基板上に形成され、さらにその酸化物薄膜の上に一般式が $ABO_3$ で示されるペロブスカイト型結晶構造の強誘電体薄膜が形成されていることを特徴とする。ただし、上記式中のAはBi、Pb、Ba、Sr、Ca、Na、K、希土類元素のうち1種又は2種以上、BはTi、Nb、Ta、W、Mo、Fe、Co、Cr、Zrのうち1種又は2種以上の元素をあらわす。

## 【特許請求の範囲】

【請求項 1】 Bi 系層状ペロブスカイト型結晶構造の酸化物薄膜が、その結晶軸の c 軸が基板面に対して垂直方向に揃うように基板上に形成され、さらにその酸化物薄膜の上に一般式が  $ABO_3$  で示されるペロブスカイト型結晶構造の強誘電体薄膜が形成されていることを特徴とする強誘電体薄膜構成体。ただし上記一般式において、

$A = Bi, Pb, Ba, Sr, Ca, Na, K$ 、希土類元素のうち 1 種又は 2 種以上

$B = Ti, Nb, Ta, W, Mo, Fe, Co, Cr, Zr$  のうち 1 種又は 2 種以上

【請求項 2】 前記の Bi 系層状ペロブスカイト型結晶構造の酸化物は下記の化学式であることを特徴とする請求項 1 記載の強誘電体薄膜構成体。

$(Bi_2O_2)^{2+} (A_{m-1} B_m O_{3m+1})^{2-}$   
ただし、

$A = Bi, Pb, Ba, Sr, Ca, Na, K$ 、希土類元素のうち 1 種又は 2 種以上

$B = Ti, Nb, Ta, W, Mo, Fe, Co, Cr$  のうち 1 種又は 2 種以上

$m = 1, 2, 3, 4, 5$

【請求項 3】 前記の強誘電体薄膜上に上部電極を形成し、基板を下部電極とした請求項 1 または 2 記載の強誘電体薄膜構成体。

【請求項 4】 前記 Bi 系層状ペロブスカイト型結晶構造の酸化物薄膜と強誘電体薄膜との間に下部電極を形成すると共に、強誘電体薄膜上に上部電極を形成してなる請求項 1 または 2 記載の強誘電体薄膜構成体。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、例えば焦電型赤外線検出素子、アクチュエータ、不揮発性かつ非破壊性のメモリなどに用いる強誘電体薄膜構成体に関するものである。

## 【0002】

【従来の技術】 一般に強誘電体は、電場がなくても自発分極  $P_s$  が存在し、その向きを外部電場によって反転させることのできる物質であり、焦電型赤外線検出素子、アクチュエータ、不揮発性かつ非破壊性のメモリ素子等に広範に応用されている。

【0003】 例えば焦電型赤外線素子は、自発分極の温度変化を利用するものであり、物質内の自発分極の向きが一方方向に揃っているときに最大限の出力を引き出すことができる。しかしながら、現在実用化されている赤外線検出素子は殆どが多結晶体のセラミックスで製造されており、結晶軸の方向が揃っていないため、分極処理をしても自発分極の向きを完全に揃えることができない。

【0004】 近年、電子部品の小型化の要求が高まっており、これを達成するために、強誘電体材料も薄膜の形

態での利用が注目されている。その際にも、自発分極  $P_s$  の方向が一方方向に揃っている強誘電体薄膜が有効とされている。例えば結晶系が正方晶である  $PbTiO_3$ 、 $Pb(Zr, Ti)O_3$ 、 $(Pb, La)TiO_3$  などの代表的な強誘電体は、結晶の c 軸方向に自発分極の方向を有するため、基板表面に対して垂直方向に結晶方位の c 軸を揃えると最大限の出力を引き出すことができる。

【0005】 上記のような強誘電体薄膜を作製する従来例として、例えば特開昭 58-186105 号公報に記載されているように、 $[100]$  面に沿ってへき開した  $MgO$  単結晶基板の下地基板の表面に、エピタキシャル成長的に形成させて製造される前記のような化学組成の強誘電体薄膜があげられる。上記のような  $MgO$  単結晶の  $[100]$  面上の格子は前記組成の強誘電体の  $[100]$  面上の格子と整合性がよいため、基板を  $550 \sim 650^\circ C$  に加熱しながらスパッタ成膜もしくは CVD 成膜すると、エピタキシャル膜が形成できる。このようにして製造された前記組成の強誘電体薄膜は、基板面に対して垂直方向に c 軸の揃った薄膜であり特性が優れている。

## 【0006】

【発明が解決しようとする問題点】 しかしながら、上記のような  $MgO$  の単結晶基板は高価であり、そのため上記の基板を用いて作製した強誘電体薄膜構成体や、さらに、その構成体から製造される電子部品や電子機器が高価になってしまう等の問題があった。

【0007】 本発明は上記の問題点を鑑みて提案されたもので、上記のような  $MgO$  単結晶基板を用いなくても、また基板の種類の如何にかかわらず、基板面に垂直に c 軸の方向が揃った強誘電体薄膜を有する強誘電体薄膜構成体を提供することを目的とする。

## 【0008】

【問題を解決するための手段】 上記の目的を達成するために本発明による強誘電体薄膜構成体は、以下の構成としたものである。

【0009】 即ち、Bi 系層状ペロブスカイト型結晶構造の酸化物薄膜が、その結晶軸の c 軸が基板面に対して垂直方向に揃うように基板上に形成され、さらにその酸化物薄膜の上に一般式が  $ABO_3$  で示されるペロブスカイト型結晶構造の強誘電体薄膜が形成されていることを特徴とする。ただし上記一般式において、

$A = Bi, Pb, Ba, Sr, Ca, Na, K$ 、希土類元素のうち 1 種又は 2 種以上

$B = Ti, Nb, Ta, W, Mo, Fe, Co, Cr, Zr$  のうち 1 種又は 2 種以上

【0010】 上記の Bi 系層状ペロブスカイト型結晶構造の酸化物としては、例えば下記の化学式で示されるものを用いる。

$(Bi_2O_2)^{2+} (A_{m-1} B_m O_{3m+1})^{2-}$

ただし、

$A = \text{Bi}, \text{Pb}, \text{Ba}, \text{Sr}, \text{Ca}, \text{Na}, \text{K}$ 、希土類元素のうち1種又は2種以上

$B = \text{Ti}, \text{Nb}, \text{Ta}, \text{W}, \text{Mo}, \text{Fe}, \text{Co}, \text{Cr}$ のうち1種又は2種以上

$m = 1, 2, 3, 4, 5$

【0011】

【作用】前述したように、強誘電体薄膜として、例えば、 $\text{PbTiO}_3$ 、 $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ 、 $(\text{Pb}, \text{La})\text{TiO}_3$ なる組成の薄膜を用いる場合、結晶方位を $c$ 軸に揃えると自発分極の向きが揃い、自発分極の温度変化を利用するような焦電型赤外線検出素子に用いる場合は最大限の出力を発揮するため都合がよい。

【0012】Bi系の層状ペロブスカイト構造を有する化合物は、低対称な構造を有し、結晶軸の $a$ 軸、 $b$ 軸方向に結晶成長しやすい特徴をもつ。基板上にこのBi系層状ペロブスカイト構造の化合物を形成すると、基板との格子整合性を持たなくても基板面方向に $a$ 軸もしくは $b$ 軸が形成されやすく、基板面の垂直方向に $c$ 軸が形成されるような膜構造をとりやすい。

【0013】一方、Bi系の層状ペロブスカイト構造化合物の $ab$ 面上の格子とペロブスカイト型 $\text{ABO}_3$ 構造の $\text{PbTiO}_3$ 、 $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ 、 $(\text{Pb}, \text{La})\text{TiO}_3$ の $ab$ 面上の格子とは整合性がよいため、このような格子整合性を持ちながらBi系層状ペロブスカイト構造化合物の $c$ 軸配向膜上にはこれらの組成の薄膜を成膜すると $c$ 軸配向しやすい。

【0014】よって、高価な $\text{MgO}$ 単結晶基板を用いなくても $c$ 軸配向性を有する特性の優れた $\text{PbTiO}_3$ 、 $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ 、 $(\text{Pb}, \text{La})\text{TiO}_3$ 等の膜を有する強誘電体薄膜構成体を作製することが可能となる。

【0015】

【実施例】以下、本発明による強誘電体薄膜構成体を、実施例に基づいて具体的に説明する。

【0016】【実施例】以下の実施例では強誘電体薄膜構成体を高周波スパッタリング法で作製した。まず、実施例1においてはBi系層状ペロブスカイト型結晶構造の酸化物薄膜として $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 薄膜をスパッタにより基板上に形成した。そのターゲット材料としては $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ の粉末と、これに対して20モル%のB

$i_2\text{O}_3$ を混合した粉末を用い、この粉末を無酸素銅製のターゲット皿に敷き詰めて表面を平にしながら押し固めてターゲットとした。スパッタの雰囲気ガスは、 $\text{Ar}$ が90%、 $\text{O}_2$ が10%の混合気体を用い、全圧は1Paとした。

【0017】基板にはコーニング7059ガラスを用い、これを基板ホルダに固定してターゲットとの距離を10cmに設定し、基板を650℃まで加熱しながら厚さ0.5 $\mu\text{m}$ の薄膜を形成した。この薄膜についてX線回折測定法による構造解析と、ICP発光分析法による組成分析を行ったところ、得られた膜は強く $c$ 軸配向している $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ であることが確認された。

【0018】次に、この $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 膜上に下部電極として0.1 $\mu\text{m}$ の白金膜を高周波スパッタ法で作製した。そのスパッタには白金板ターゲットを用い、そのターゲットと基板との距離を10cmとし、基板を600℃に加熱して $\text{Ar}$ ガス雰囲気中で全圧0.5Paの条件で行った。

【0019】さらに、上記の下部電極の上に、次の条件で $\text{PbTiO}_3$ 薄膜をスパッタにより作製した。ターゲット材料には、 $\text{PbTiO}_3$ に20モル%の $\text{PbO}$ を混合した粉末を用い、これを無酸素銅製のターゲット皿に敷き詰めて表面を平に押し固めてターゲットとした。スパッタ雰囲気は $\text{Ar}$ が90%、 $\text{O}_2$ が10%の混合気体を用いて全圧を1Paとし、基板を620℃に加熱して厚さ1.0 $\mu\text{m}$ の $\text{PbTiO}_3$ 薄膜を形成した。

【0020】上記のようにして得られた薄膜の結晶構造および組成を、X線回折測定法およびICP発光分析法で調べたところ、 $c$ 軸配向性の強い $\text{PbTiO}_3$ 膜が作製されていることがわかった。またX線回折ピーク強度から下記の式を用いて $c$ 軸配向率 $\alpha$ (%)を算出したところ、95%であった。

$$\alpha = \{ I_{001} / (I_{001} + I_{100} + I_{101} + I_{110} + I_{111}) \} \times 100$$

【0021】次に実施例2～9として、上記実施例1とほぼ同様の要領で、基板およびBi系層状ペロブスカイト型結晶構造酸化物の組成を変えて、種々の組成の強誘電体薄膜を作製し、それらの $c$ 軸配向率を調べた。以上の結果を下記表1にまとめて示す。

【0022】

表 1

実施例	基 板	Bi系層状ペロブスカイト酸化物の組成	強誘電体 薄膜	c軸配向率 $\alpha$
1	7059ガラス	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{PbTiO}_3$	95
2	7059ガラス	$\text{PbBi}_2\text{Nb}_2\text{O}_9$	$\text{PbTiO}_3$	93
3	7059ガラス	$\text{Sr}_{0.8}\text{Bi}_{1.2}\text{Ti}_{0.2}\text{Nb}_{1.8}\text{O}_9$	$\text{PbTiO}_3$	92
4	7059ガラス	$\text{PbBi}_4\text{Ti}_4\text{O}_{15}$	$\text{PbTiO}_3$	95
5	7059ガラス	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$	95
6	SUS 304	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{PbTiO}_3$	97
7	Si(110)	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{PbTiO}_3$	95
8	Si(110)	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$	95
9	アルミナ	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{PbTiO}_3$	97

【0023】〔比較例〕上記実施例に対する比較例としてコーニング7059ガラス上に下地膜としてBi系の層状ペロブスカイト酸化物を形成することなく、強誘電体薄膜を形成した場合と、従来の【100】面でへき開

したMgO単結晶基板上に強誘電体薄膜を成膜した場合のc軸配向率を下記表2に示す。

【0024】

表 2

比較例	基 板	Bi系層状ペロブスカイト酸化物の組成	強誘電体 薄膜	c軸配向率 $\alpha$
1	7059ガラス	なし	$\text{PbTiO}_3$	15
2	(100)MgO単結晶	なし	$\text{PbTiO}_3$	91

【0025】上記表2中の比較例1に示したように、基板としてコーニング7059ガラスを用い、その基板上に下地膜としてBi系の層状ペロブスカイト酸化物を形成することなく強誘電体薄膜を成膜した場合のc軸配向率は非常に低いのにに対し、本発明による前記各実施例のようにBi系層状ペロブスカイト酸化物を下地膜として設けると、その表面に前記表1のようにc軸配向率の高い強誘電体薄膜を形成することができる。しかも、その各実施例のc軸配向率 $\alpha$ は、上記表2の比較例2で示した従来の高価なMgO単結晶基板を用いた場合と同等か、もしくはそれ以上であり、極めて配向率のよい強誘電体薄膜を形成できるものである。

【0026】その結果、本発明による強誘電体薄膜構成体は、焦電型赤外線検出素子やアクチュエータ等に有用な特性のよい強誘電体素子として用いることができる。この場合、電極は強誘電体薄膜の両側に設けるもので、上記実施例のようにBi系層状ペロブスカイト型結晶構造の酸化物薄膜の上に下部電極と強誘電体薄膜とを順に形成した後に、強誘電体薄膜上に上部電極を形成する。或いは強誘電体薄膜上に上部電極を形成し、基板を下部

電極として利用することもできる。その場合、強誘電体薄膜は、上記の酸化物薄膜の上に、実施例のような下部電極を形成することなく成膜するものであるが、そのような場合にも配向率の高い強誘電体薄膜を形成できることは勿論である。

【0027】

【発明の効果】以上詳述したように、本発明による強誘電体薄膜構成体は、Bi系層状ペロブスカイト型結晶構造の酸化物薄膜が、その結晶軸のc軸が基板に垂直方向に揃うように基板上に配置され、さらにその上に一般式が $\text{ABO}_3$ で示されるペロブスカイト型結晶構造の強誘電体薄膜が配置された構成としたから、従来のように下地基板として高価なMgO単結晶基板を用いることなく、安価な他の基板を用いて、MgO単結晶基板を用いた場合と同等もしくはそれよりもc軸配向性のよい強誘電体薄膜を有する構成体が得られる。その結果、焦電型赤外線検出素子やアクチュエータあるいは不揮発性かつ非破壊性のメモリなどの電子部品を安価に製造できる等の効果がある。

## PATENT ABSTRACTS OF JAPAN

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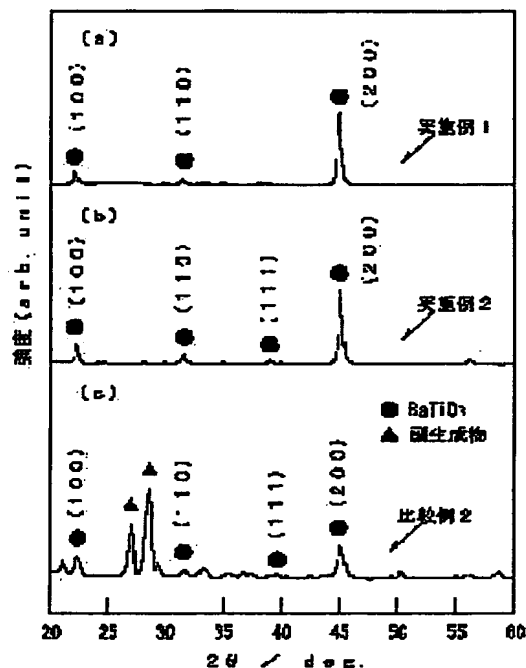
(72)Inventor : TANI TOSHIHIKO  
KIMURA TOSHIO

## (54) METHOD OF MANUFACTURING CRYSTAL-ORIENTED CERAMIC

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a method of manufacturing crystal-oriented ceramics where crystal-oriented ceramics consisting of an isotropic perovskite-type compound and having a high degree of orientation can be manufactured and where the composition of A-site elements contained in the crystal-oriented ceramics can be easily controlled.

**SOLUTION:** A plate-like powder which consists of a bismuth-layered titanate compound and whose developed faces have a lattice matching with the pseudo-cubic {100} face of the isotropic perovskite-type compound is mixed with a perovskite-forming raw material which reacts with the above plate-like powder to produce the isotropic perovskite-type compound and surplus components including a bismuth oxide (a mixing process). Next, the mixture is so molded that the plate-like powder is oriented (a molding process). Furthermore, the plate-like powder included in the resultant mold is made to react with the perovskite-forming raw material and on/after the reaction, the surplus components produced by the reaction are thermally/chemically removed (a reacting and removing process).



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(71)Applicant : SUMITOMO METAL MINING CO LTD

(22)Date of filing : 10.03.1995

(72)Inventor : ABE TAKAYUKI

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## (54) FERROELECTRIC THIN FILM CONSTITUTION BODY

### (57)Abstract:

PURPOSE: To obtain a ferroelectric thin-film constitution body having a ferroelectric thin film having the properly arranged c-axis direction perpendicular to the surface of a substrate regardless of the kind thereof even without using a conventional expensive MgO single crystal substrate in relation to a ferroelectric thin-film constitution body used in, e.g. a pyroelectric type infrared detecting element, an actuator or a nonvolatile and nondestructive memory.

CONSTITUTION: This ferroelectric thin-film constitution body is obtained by forming an oxide thin film of a Bi-based layer perovskite type crystal structure on a substrate so as to properly arrange the (c)-axis of the crystal axis in the direction perpendicular to the substrate surface and further forming a ferroelectric thin film having the perovskite type crystal structure represented by the general formula  $ABO_3$  (A denotes one or more of Bi, Pb, Ba, Sr, Ca, Na, K and rare earth elements; B denotes one or more of Ti, Nb, Ta, W, Mo, Fe, Co, Cr and Zr) on the resultant oxide thin film.

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CLAIMS

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[Claim(s)]

[Claim 1] The oxide thin film of Bi system stratified perovskite mold crystal structure is formed on a substrate so that the c-axis of the crystallographic axis may gather perpendicularly to a substrate side, and a general formula is  $ABO_3$  on the oxide thin film further. Ferroelectric thin film construct characterized by forming the ferroelectric thin film of the perovskite mold crystal structure shown. However, it sets to the above-mentioned general formula, and is one sort or two sorts or more in one sort or two or more sort  $B=Ti$ , and Nb, Ta, W, Mo, Fe, Co, Cr and Zr in  $A=Bi$ , Pb, Ba, Sr, calcium, Na and K, and rare earth elements [claim 2]. The oxide of the aforementioned Bi system stratified perovskite mold crystal structure is a ferroelectric thin film construct according to claim 1 characterized by being the following chemical formula.

$(Bi\ 2O_2)$  the inside of  $2+(Am-1\ Bm\ O_{3m+1})_2$ - however  $A=Bi$ , Pb, Ba, Sr, calcium, Na and K, and rare earth elements -- the inside of one sort or two or more sort  $B=Ti$ , and Nb, Ta, W, Mo, Fe, Co and Cr -- one sort or more than 2 sort  $m=1$ , and 2, 3, 4 and 5 -- [Claim 3] The ferroelectric thin film construct according to claim 1 or 2 which formed the up electrode on the aforementioned ferroelectric thin film, and used the substrate as the lower electrode.

[Claim 4] The ferroelectric thin film construct according to claim 1 or 2 which comes to form an up electrode on a ferroelectric thin film while forming a lower electrode between the oxide thin film of said Bi system stratified perovskite mold crystal structure, and a ferroelectric thin film.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the ferroelectric thin film construct used for the memory of for example, a pyroelectric infrared detector, an actuator, a non-volatile, and un-destroying nature etc.

[0002]

[Description of the Prior Art] Generally, a ferroelectric is spontaneous polarization PS, even if there are no electric field. It exists, and it is the matter which can reverse the sense by external electric field, and is extensively applied to the memory device of a pyroelectric material mold infrared detector, an actuator, a non-volatile, and un-destroying nature etc.

[0003] For example, a pyroelectric infrared component uses the temperature change of spontaneous polarization, and when the sense of the spontaneous polarization in the matter is equal to the one direction, it can pull out the maximum output. However, most is manufactured with the ceramics of the polycrystalline substance, and since the direction of a crystallographic axis has not gathered, even if the infrared detector put in practical use now carries out polarization processing, it cannot arrange the sense of spontaneous polarization completely.

[0004] In recent years, the demand of a miniaturization of electronic parts is increasing, and in order to attain this, use with the gestalt of a thin film attracts attention also into the ferroelectric ingredient. Also in that case, it is spontaneous polarization PS. The direction is confirmed by the ferroelectric thin film which is equal to the one direction. for example,  $\text{PbTiO}_3$  whose crystal system is \*\*\*\*\*,  $\text{Pb}(\text{Zr}, \text{Ti}) \text{O}_3$ , and  $\text{TiO}(\text{Pb}, \text{La})_3$  etc. -- since a typical ferroelectric has the direction of spontaneous polarization in the direction of a c-axis of a crystal, if the c-axis of crystal orientation is perpendicularly arranged to a substrate front face, it can pull out the maximum output.

[0005] As a conventional example which produces the above ferroelectric thin films, the ferroelectric thin film of the above chemical composition which is made to form in the front face of the substrate substrate of the  $\text{MgO}$  single crystal substrate which carried out the cleavage along  $\{100\}$  sides in epitaxial growth, and is manufactured is raised as described at JP,58-186105,A. Since the grid on the  $\{100\}$  sides of the above  $\text{MgO}$  single crystals has good grid and adjustment on the  $\{100\}$  sides of the ferroelectric of said presentation, if it forms [ spatter-] membranes or forms [ CVD-] membranes, heating a substrate at 550-650 degrees C, it can form an epitaxial film. Thus, the ferroelectric thin film of said manufactured presentation is a thin film with which the c-axis gathered perpendicularly to the substrate side, and the property is excellent.

[0006]

[Problem(s) to be Solved by the Invention] However, the above single crystal substrates of  $\text{MgO}$  had the problem of the ferroelectric thin film construct, the electronic parts further manufactured from the construct, and electronic equipment which were produced at an expensive price therefore using the above-mentioned substrate becoming expensive.

[0007] Even if this invention was not proposed in view of the above-mentioned trouble and does not use the above  $\text{MgO}$  single crystal substrates, it aims at offering the ferroelectric thin film construct which has the ferroelectric thin film to which the direction of a c-axis was equal at right angles to a substrate side regardless of the class of substrate.

[0008]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the ferroelectric thin film construct by this invention is taken as the following configurations.

[0009] That is, the oxide thin film of Bi system stratified perovskite mold crystal structure is formed on a substrate so that the c-axis of the crystallographic axis may gather perpendicularly to a substrate side, and a

general formula is  $ABO_3$  on the oxide thin film further. It is characterized by forming the ferroelectric thin film of the perovskite mold crystal structure shown. However, it sets to the above-mentioned general formula, and is one sort or two sorts or more in one sort or two or more sort  $B=Ti$ , and  $Nb$ ,  $Ta$ ,  $W$ ,  $Mo$ ,  $Fe$ ,  $Co$ ,  $Cr$  and  $Zr$  in  $A=Bi$ ,  $Pb$ ,  $Ba$ ,  $Sr$ , calcium,  $Na$  and  $K$ , and rare earth elements [0010]. What is shown, for example with the following chemical formula as an oxide of the above-mentioned  $Bi$  system stratified perovskite mold crystal structure is used.

( $Bi\ 2O_2$ ) It is one sort or more than 2 sort  $m=1$ , and 2, 3, 4 and 5 [0011] among one sort or two or more sort  $B=Ti$ , and  $Nb$ ,  $Ta$ ,  $W$ ,  $Mo$ ,  $Fe$ ,  $Co$  and  $Cr$  among  $2+(Am-1\ Bm\ O_{3m+1})_2$ - however  $A=Bi$ ,  $Pb$ ,  $Ba$ ,  $Sr$ , calcium,  $Na$  and  $K$ , and rare earth elements.

[Function] As mentioned above, they are  $PbTiO_3$ ,  $Pb(Zr, Ti)\ O_3$ , and  $TiO(Pb, La)_3$  as a ferroelectric thin film. It is convenient in order to demonstrate the maximum output, when using for a pyroelectric infrared detector for which the sense of spontaneous polarization will use the temperature change of a set and spontaneous polarization if crystal orientation is arranged with a c-axis when using the thin film of a presentation.

[0012] The compound which has the stratified perovskite structure of  $Bi$  system has structure symmetrical with low, and has the description which is easy to carry out crystal growth in the a-axis of a crystallographic axis, and the direction of a b-axis. If the compound of this  $Bi$  system stratified perovskite structure is formed on a substrate, it will be easy to take membrane structure by which is [ an a-axis or a b-axis ] easy to be formed in the direction of a substrate side even if it does not have grid adjustment with a substrate, and a c-axis is formed in the perpendicular direction of a substrate side.

[0013] On the other hand, it is the grid and the perovskite mold  $ABO_3$  on the a-b plane of the stratified perovskite structure compound of  $Bi$  system.  $PbTiO_3$  of structure,  $Pb(Zr, Ti)\ O_3$ , and  $TiO_3(Pb, La)$  Since the grid on a-b plane has good adjustment, if the thin film of these presentations is formed on the c-axis orientation film of  $Bi$  system stratified perovskite structure compound, having such grid adjustment, it will be easy to carry out c-axis orientation.

[0014] therefore,  $PbTiO_3$  which was excellent in the property of having a c-axis stacking tendency even if it did not use an expensive  $MgO$  single crystal substrate,  $Pb(Zr, Ti)\ O_3$ , and  $TiO(Pb, La)_3$  etc. -- it becomes possible to produce the ferroelectric thin film construct which has the film.

[0015]

[Example] Hereafter, the ferroelectric thin film construct by this invention is concretely explained based on an example.

[0016] [Example] -- in the following examples, the ferroelectric thin film construct was produced by the RF-sputtering method. First, in the example 1,  $3OBi_4\ Ti_{12}$  thin film was formed on the substrate by the spatter as an oxide thin film of  $Bi$  system stratified perovskite mold crystal structure. Having covered the target pan made from oxygen free copper with this powder using the powder of  $Bi_4\ Ti\ 3O_{12}$ , and the powder which mixed 20-mol % of  $Bi\ 2O_3$  to this, and making a front face into Taira as that target ingredient, it pushed and hardened and considered as the target. For the controlled atmosphere of a spatter,  $Ar$  is 90% and  $O_2$ . Total pressure was set to 1Pa using 10% of mixture of gas.

[0017] This was fixed to the substrate at the substrate holder using Corning 7059 glass, distance with a target was set as 10cm, and the thin film with a thickness of 0.5 micrometers was formed, heating a substrate to 650 degrees C. When structural analysis by the X diffraction measuring method and the component analysis by the ICP AEM method were performed about this thin film, it was checked that the obtained film is  $Bi_4\ Ti\ 3O_{12}$  which is carrying out c-axis orientation strongly.

[0018] Next, the 0.1-micrometer platinum film was produced by the RF spatter as a lower electrode on this  $Bi_4\ Ti_3\ O_{12}$  film. Distance of the target and substrate was set to 10cm at the spatter using the platinum plate target, the substrate was heated at 600 degrees C, and it carried out on conditions with a total pressure of 0.5Pa in  $Ar$  gas ambient atmosphere.

[0019] Furthermore, it is  $PbTiO_3$  at the following conditions on the above-mentioned lower electrode. The thin film was produced by the spatter. In a target ingredient, it is  $PbTiO_3$ . Using the powder which mixed 20-mol % of  $PbO$ , the target pan made from oxygen free copper was covered with this, the front face was pushed on Taira, was hardened, and it considered as the target. For a spatter ambient atmosphere,  $Ar$  is 90% and  $O_2$ . Total pressure is set to 1Pa using 10% of mixture of gas, a substrate is heated at 620 degrees C, and it is  $PbTiO_3$  with a thickness of 1.0 micrometers. The thin film was formed.

[0020] When the crystal structure of a thin film and the presentation which were acquired as mentioned above were investigated by the X diffraction measuring method and the ICP AEM method, it is strong  $PbTiO_3$  of a c-axis stacking tendency. It turned out that the film is produced. Moreover, it was 95% when

rate of c-axis orientation  $\alpha$  (%) was computed using the following formula from X diffraction peak intensity.

$\alpha = \{I_{001}/(I_{001}+I_{100}+I_{101}+I_{110}+I_{111})\} \times 100$  [0021] Next, as examples 2-9, in the almost same way as the above-mentioned example 1, the presentation of a substrate and Bi system stratified perovskite mold crystal structure oxide was changed, the ferroelectric thin film of various presentations was produced, and those rates of c-axis orientation were investigated. The above result is collectively shown in the following table 1.

[0022]

表 1

実施例	基 板	B i 系層状ペロブスカイト酸化物の組成	強誘電体薄膜	c 軸配向率 $\alpha$
1	7059ガラス	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{PbTiO}_3$	9 5
2	7059ガラス	$\text{PbBi}_2\text{Nb}_2\text{O}_9$	$\text{PbTiO}_3$	9 3
3	7059ガラス	$\text{Sr}_{0.8}\text{Bi}_{1.2}\text{Ti}_{0.2}\text{Nb}_{1.8}\text{O}_9$	$\text{PbTiO}_3$	9 2
4	7059ガラス	$\text{PbBi}_4\text{Ti}_4\text{O}_{15}$	$\text{PbTiO}_3$	9 5
5	7059ガラス	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$	9 5
6	SUS 304	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{PbTiO}_3$	9 7
7	Si(110)	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{PbTiO}_3$	9 5
8	Si(110)	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$	9 5
9	アルミナ	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{PbTiO}_3$	9 7

[0023] [Example of a comparison] It is Bi as substrate film on Corning 7059 glass as an example of a comparison over the above-mentioned example. The rate of c-axis orientation the case where a ferroelectric thin film is formed, and at the time of forming a ferroelectric thin film on the MgO single crystal substrate which carried out the cleavage in respect of conventional {100} is shown in the following table 2, without forming the stratified perovskite oxide of a system.

[0024]

表 2

比較例	基 板	B i 系層状ペロブスカイト酸化物の組成	強誘電体薄膜	c 軸配向率 $\alpha$
1	7059ガラス	なし	$\text{PbTiO}_3$	1 5
2	(100)MgO単結晶	なし	$\text{PbTiO}_3$	9 1

[0025] As shown in the example 1 of a comparison in the above-mentioned table 2, Corning 7059 glass is used as a substrate. It is Bi as substrate film on the substrate. As opposed to a thing with the very low rate of c-axis orientation at the time of forming a ferroelectric thin film, without forming the stratified perovskite oxide of a system If Bi system stratified perovskite oxide is prepared as substrate film like said each example by this invention, as shown in said table 1, a ferroelectric thin film with the high rate of c-axis orientation can be formed in the front face. and the case where the rate  $\alpha$  of c-axis orientation of each of that example uses the expensive conventional MgO single crystal substrate shown in the example 2 of a comparison of the above-mentioned table 2 and an EQC -- or it is more than it and a ferroelectric thin film with the very sufficient rate of orientation can be formed.

[0026] Consequently, the ferroelectric thin film construct by this invention can be used as a ferroelectric component with the useful sufficient property to a pyroelectric infrared detector, an actuator, etc. In this case, after it prepares an electrode in the both sides of a ferroelectric thin film and it forms a lower electrode and a ferroelectric thin film in order like the above-mentioned example on the oxide thin film of Bi system stratified perovskite mold crystal structure, it forms an up electrode on a ferroelectric thin film. Or an up

electrode can be formed on a ferroelectric thin film, and a substrate can also be used as a lower electrode. In that case, although a ferroelectric thin film forms membranes, without forming a lower electrode like an example on the above-mentioned oxide thin film, it is natural. [ of the ability of a ferroelectric thin film with the high rate of orientation to be formed in such a case ]

[0027]

[Effect of the Invention] As explained in full detail above, the ferroelectric thin film construct by this invention The oxide thin film of Bi system stratified perovskite mold crystal structure is arranged on a substrate so that the c-axis of the crystallographic axis may be perpendicularly equal to a substrate. Furthermore, a general formula is  $ABO_3$  on it. Since it considered as the configuration by which the ferroelectric thin film of the perovskite mold crystal structure shown has been arranged The construct which has the good ferroelectric thin film of a c-axis stacking tendency is obtained using other cheap substrates rather than the case where a MgO single crystal substrate is used, an EQC, or it, without using a MgO single crystal substrate expensive as a substrate substrate like before. Consequently, there is effectiveness of being able to manufacture cheaply electronic parts, such as a pyroelectric infrared detector and memory of an actuator or a non-volatile, and un-destroying nature.

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[Translation done.]